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Translated from German by the Ralph McElroy Co., Custom Division  
P.O. Box 4828, Austin, Texas 78765 USA

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## PREPARATION OF 1,2-PROPANEDIOL FROM GLYCERIN

Applicant:

Henkel KGaA,  
40589 Düsseldorf, DE

Inventors:

Dr. Theo Fleckenstein  
4010 Hilden, DE;

Dr. Gerd Göbel  
5000 Köln, DE

Dr. Franz-Josef Carduck  
5657 Haan, DE

Glycerin is continuously hydrogenated in the presence of a heterogeneous catalyst that contains a metal element, a metal salt, a metal oxide, and/or another metal compound and/or alloy from Groups I and/or VIII, with diluted or nondiluted hydrogen at pressures of 20-300 bar, particularly 100-250 bar, and at temperatures of 150-320°C to form 1,2-propanediol. Here, glycerin is passed over a fixed bed of catalyst in vapor or liquid form. A process is thereby made available that can be used on a large scale for the production of 1,2-propanediol from renewable raw materials.

#### Description

The invention pertains to a process for the preparation of 1,2-propanediol (propylene glycol). 1,2-propanediol is produced today on a large scale from propylene oxide (propene oxide) by the addition of water. It is used in a multitude of applications, especially in the foodstuffs industry, as a solvent for dyes and aromatics, as a moisture retaining agent for tobacco, in cosmetics, as a component of brake and hydraulic fluids, as an antifreeze, as a lubricant in refrigeration equipment, [and] as a solvent for fats, oils, resins, waxes, dyes, etc. It also serves as the starting material for the preparation of other products. By esterification and/or etherification, numerous usable products are obtained that can be used as solvents for syntheses, [and] as plasticizers, thickeners, emulsifiers, etc.

Nearly the entire [amount] of propylene glycol presently marketed is produced from fossil raw materials, namely, from natural gas and crude oil in the final analysis. However, in light of the worldwide trend toward the use of renewable raw materials, there is a need for 1,2-propanediol made from regenerable materials. Especially for the use of 1,2-propanediol in foods and edibles as well as in the cosmetics and pharmaceuticals area, an increasingly stronger demand can be expected for products derived from natural raw materials. This trend also exists for substances synthesized from 1,2-propanediol.

Although a process is known from European Patent No. 254,189 A2 or the corresponding U.S. Patent No. 4,982,020 which, starting with natural oils and fats, describes the preparation of 1,2-propanediol, what is involved here is a process for the preparation of fatty alcohols from triglycerides by hydrogenation wherein 1,2-propanediol is additionally produced in high yields.

The hydrogenation of glycerin to propylene glycol has also been known for a long time and is described in, e.g., Z. physikal. Chem. Abt. A 159 (1932) 352 and J. Amer. Chem. Soc. 54 (1932) 4680. The process is described individually and in more detail in German Patent Nos. 524,101 and 541,362 from the year 1931. Thus, according to German Patent No. 524,101, glycerin is hydrogenated to form 1,2-propanediol and propanol over a copper chromate contacting agent at a temperature of 200-210°C in a laboratory experiment. The yield of 1,2-propanediol is up to 70%. According to German Patent No. 541,362, glycerin is hydrogenated to form 1,2-propanediol at 200-240°C and 100 bar in the presence of a nickel catalyst. However, in these cases, experiments on a laboratory scale are

involved without the suitability for large-scale [production] being proven.

It is the goal of the invention to develop a process that can be used on a large scale for the preparation of 1,2-propanediol from renewable raw materials.

This goal is attained by the invention in that glycerin is continuously hydrogenated in the presence of a heterogeneous catalyst that contains a metal element, a metal salt, a metal oxide, and/or another metal compound and/or alloy from Groups I and/or VIII, with diluted or nondiluted hydrogen at pressures of 20-300 bar, especially 100-250 bar, and temperatures of 150-320°C to form 1,2-propanediol, wherein glycerin is passed over a fixed bed of catalyst in vapor or liquid form. An additional advantage of the process of the invention lies in the possibility of recovering propanediol, which in the long term is becoming more valuable compared to glycerin, from glycerin. It can be expected namely that the value of glycerin will fall below that of 1,2-propanediol in the long run.

The reaction, which proceeds by the splitting off of water, can be done with high degrees of conversion and high selectivity.

As catalysts, integral or supported contacting agents are involved that contain metals, metal salts, metal oxides, or the like from Groups I and VIII as main components. Additional metals can be added dosewise to improve the properties.

Here, the catalyst can be prepared in various ways. To name only a few examples, precipitation of the metal salts, impregnation, ion exchange, or solid state reactions can be considered.

As catalysts, the hydrogenation catalysts, e.g., those that find application in the preparation of fatty alcohols from fatty acid methyl esters or in the hardening of fatty acids, and are known in and of themselves, can be used. However, it is especially proposed that the process be done with catalysts containing copper as an active component, specifically, e.g., in the form of Cu chromite, Cu-zinc oxide, Cu-aluminum oxide, or Cu-silicon dioxide.

The Cu chromite preferably used contains 30-40 wt% of copper [and] 23-30 wt% of chromium, based in each case on the oxidic catalyst mass, as well as additional transition metals in the form of their oxides if desired. Here, it is advantageous if the catalyst contains 1-7 wt%, especially 1.5-3 wt%, of barium, based on the oxidic catalyst mass. In an especially advantageous embodiment, the catalyst contains 32-38 wt% of copper, based on the oxidic catalyst mass, 26-30 wt% of chromium, 1.5-3 wt% of barium, 0.5-2 wt% of silicon, and additionally, 1-5 wt% each, preferably 2-3 wt%, of manganese, zirconium, and/or cerium, based on the oxidic catalyst mass. This catalyst and the process for its preparation is extensively described in European Patent No. 254,189 A2. Express reference is made here to the disclosure given there; the information given there should also be [considered] a component of the present application. However, the invention is not restricted to Cu chromite catalysts. Other catalysts, e.g., Cu/ZnO or Cu/Al<sub>2</sub>O<sub>3</sub>, can also be used.

It is important and preferred that the catalyst have a high surface area and porosity so that a high activity and selectivity as well as a high service life, which is especially important for technical applications, can be obtained. Thus, it is advantageous

if the catalyst used has a specific surface area of 20-80 m<sup>2</sup>/g, preferably 25-70 m<sup>2</sup>/g, as well as a pore volume of 0.1-1.0 cm<sup>3</sup>/g.

The Cu-ZnO catalyst used in Examples 3-8 is described in "Journal für praktische Chemie," 4th Series, Vol. 15, 1962. The Cu-Al<sub>2</sub>O<sub>3</sub> catalyst is commercially available from Mallinckrodt [under the trade name] Calsicat. The characteristics data for both catalysts are summarized in the form of a table below.

The reaction itself can be done in reactors that are similar to conventional and known ones for the preparation of fatty alcohols by the hydrogenation of fatty acid methyl esters or directly from triglycerides. It is advantageous if the hydrogenation is done in isothermally operated tube reactors or tube bundle reactors. The reaction parameters of temperature and pressure can be adjusted to the respective catalyst activity in each case. The heat of reaction is for the most part removed via the reactor walls so that a practically isothermal mode of operation is possible. With this manner of performing the process, the hydrogenation reaction can be controlled in such a manner that the reaction is stopped at the stage of the desired reaction product. It is especially suggested that liquid glycerin be passed in a cocurrent or countercurrent manner over a fixed bed of catalyst with hydrogen in a trickling process, also called "trickle-bed."

Optimal hydrogenation results can be obtained if glycerin is passed, without back-mixing, through the bulk of the catalyst or the reaction tube(s) at a defined residence time.

In performing the reaction, a mole ratio of hydrogen to glycerin of 2-500 in particular is used, with the excess hydrogen being recirculated.

A high-purity product free of propylene oxide and polymer is obtained with the process of the invention. For processing, water is removed from the reaction mixture obtained; if desired, additional processing steps can be done.

Examples of the process of the invention are described in more detail below, which document the suitability of the process on a technical scale. However, the invention is not restricted to these.

#### Examples 1 and 2

A 2-m-long reaction tube with an inside diameter of 25 mm was filled with copper chromite pellets (1/8" x 1/8") prepared according to Example 1 of U.S. Patent No. 4,982,020, which are also suitable for the hydrogenation of glycerin to form solid alcohols and 1,2-propanediol. Initially, [the catalyst] was activated with 1% hydrogen in nitrogen and subsequently [glycerin] was hydrogenated at 200 bar.

The results are summarized in Table I.



Table I. Analysis results of the reaction mixture from the fixed-bed hydrogenation of glycerin

Catalyst: Cu-chromite, pellets (1/8" x 1/8")

① Beispiel	1	2
② Reaktionstemperatur (°C)	225	270
③ Belastung an Glycerin (1/1 h)	0,25	0,5
④ Reaktionsdruck (bar)	200	200
⑤ Molares Wasserstoff/Glycerin-Verhältnis	25 : 1	25 : 1
<u>⑥ Produktzusammensetzung</u> (in Gew.-%)		
Glycerin	23,5	< 0,1
⑦ 1,2 Propandiol	54,2	42,2
n-Propanol	n.n.	9,8
i-Propanol	1,0	3,8
Ethanol	0,9	2,8
Methanol	1,3	3,5
⑧ unbekannt	1,0	1,0
⑨ Wasser	18,1	36,8

⑩ n.n.: nicht nachweisbar

Key:	1	Example
	2	Reaction temperature
	3	Glycerin loading
	4	Reaction pressure
	5	Hydrogen/glycerin mole ratio
	6	Product composition (in wt%)
	7	1,2-propanediol
	8	Unknown
	9	Water
	10	Not detected

#### Examples 3-8

The experiments were done with a tube reactor as in Examples 1 and 2. A Cu/ZnO catalyst in the form of 4 mm x 4 mm pellets was used. The experimental conditions and results are given in Table II.

#### Examples 9-10

These experiments were also done with a tube reactor as in Examples 1 and 2. A Cu/Al<sub>2</sub>O<sub>3</sub> catalyst from Mallinckrodt, Calsicat [trade name] was used in the form of 1/8" x 1/8" pellets. The experimental conditions and results are summarized in Table III.

The characteristics data of the catalysts used in Examples 3-10 are summarized in Table IV.

Table II. Experimental conditions and analysis results for the fixed-bed hydrogenation of glycerin

Beispiel	3	4	5	6	7	8
Reaktionstemperatur °C	180	200	220	240	240	240
LHSV (Glycerin), 1/h	0,5	0,5	0,5	0,5	0,5	0,5
Reaktionsdruck, bar	250	250	250	250	150	50
Wasserstoff/Glycerin, mol/mol	130	130	130	130	130	130
<u>Produktzusammensetzung,</u>						
Gew.-%						
Glycerin	35,9	<0,1	<0,1	<0,1	<0,1	<0,1
1,2-Propandiol	47,8	68,4	64,9	34,9	31,1	22,7
n-Propandiol	0,1	0,4	0,9	2,8	2,6	3,1
i-Propandiol	0,1	0,2	0,6	2,6	2,8	1,9
Methanol	1,1	1,8	1,4	2	1,5	1,2
Ethanol	0,1	0,3	0,6	1,6	1,7	1,6
Hydroxyacetone	0,1	0	0	0	0,1	0,2
Unbekannt	0,05	5,4	7,4	22,8	25,5	34
Wasser	14,75	23,5	24,2	33,3	34,7	35,3

Key: 1 Example  
 2 Reaction temperature  
 3 Reaction pressure  
 4 Hydrogen/glycerin [ratio]  
 5 Product composition (in wt%)  
 6 Hydroxyacetone  
 7 Unknown  
 8 Water

Table III. Experimental conditions and analysis results for the fixed-bed hydrogenation of glycerin

① Beispiel	9	10
② Reaktionstemperatur °C	220	240
LHSV (Glycerin), 1/h	1	1
③ Reaktionsdruck, bar	250	250
④ Wasserstoff/Glycerin, mol/mol	130	130
⑤ <u>Produktzusammensetzung,</u>		
Gew.-%		
Glycerin	8,2	<0,1
1,2-Propandiol	66,5	62,2
n-Propandiol	0,7	3,2
i-Propandiol	0,3	2,1
Methanol	1,3	1,8
Ethanol	0,2	0,7
⑥ Hydroxyacetone	0,1	0,2
⑦ unbekannt	1,5	5,3
⑧ Wasser	21,2	24,5

- Key: 1 Example  
 2 Reaction temperature  
 3 Reaction pressure  
 4 Hydrogen/glycerin [ratio]  
 5 Product composition (in wt%)  
 6 Hydroxyacetone  
 7 Unknown  
 8 Water

Table IV. Catalyst characteristics

① Typ	Cu/ZnO	Cu/Al <sub>2</sub> O <sub>3</sub>
② Kupfergehalt (berechnet als CuO in Gew.-%)	35 - 40	80 - 88
Form	Tabletten ③	Tabletten ③
③ Größe, mm	4 x 4	3,2 x 3,2
④ Schüttgewicht kg/l	1,2 - 1,4	1,6 - 2,0
⑤ spez. Oberfläche (BET, m <sup>2</sup> /g)	55 - 70	45 - 55
⑥ Porenvolumen, cm <sup>3</sup> /g	0,29 - 0,42	0,1 - 0,18
⑦ mittlerer Porenradius, nm	15 - 25	13 - 19

Key: 1      Type  
2      Copper content (calculated as CuO in wt%)  
3      Size  
4      Bulk density  
5      Spec. surface area  
6      Pore volume  
7      Average pore radius  
8      Pellets

### Claims

1. Process for preparation of 1,2-propanediol, characterized by the fact that glycerin is continuously hydrogenated in the presence of a heterogeneous catalyst that contains a metal element, a metal salt, a metal oxide, and/or another metal compound and/or alloy from Groups I and/or VIII, with diluted or nondiluted hydrogen at pressures of 20-300 bar, especially 100-250 bar, and at temperatures of 150-320°C, to form 1,2-propanediol, wherein glycerin is passed over a fixed bed of catalyst in vapor or liquid form.

2. Process according to Claim 1, characterized by the fact that the process is done with copper-containing catalysts.

3. Process according to Claim 2, characterized by the fact that catalysts are used that contain 30-40 wt% of copper [and] 23-30 wt% of chromium, based in each case on the oxidic catalyst mass, as well as possibly additional transition metals in the form of their oxides.

4. Process according to Claim 3, characterized by the fact that the catalyst additionally contains 1-7 wt%, especially 1.5-3 wt%, of barium, based on the oxidic catalyst mass.

5. Process according to Claim 4, characterized by the fact that the catalyst contains 32-38 wt% of copper, based on the oxidic catalyst mass, 26-30 wt% of chromium, 1.5-3 wt% barium, 0.5-2 wt% of silicon, and additionally, 1-5 wt% each, preferably 2-3 wt%, of manganese, zirconium, and/or cerium, based on the oxidic catalyst mass.

6. Process according to Claim 1 or 2, characterized by the fact that a Cu/ZnO catalyst is used.

7. Process according to Claim 1 or 2, characterized by the fact that a Cu/Al<sub>2</sub>O<sub>3</sub> catalyst is used.

8. Process according to one of Claims 1-7, characterized by the fact that the catalyst used has a specific surface area in the range of 20-80 m<sup>2</sup>/g, preferably 25-70 m<sup>2</sup>/g.

9. Process according to one of Claims 1-8, characterized by the fact that the catalyst used has a pore volume of 0.1-1.0 cm<sup>3</sup>/g.

10. Process according to one of Claims 1-9, characterized by the fact that the hydrogenation is done in an isothermally operated tube reactor or in a tube bundle reactor.

11. Process according to one of Claims 1-10, characterized by the fact that liquid glycerin is passed in a cocurrent or countercurrent manner with hydrogen over the fixed bed of catalyst in a trickling process ("trickle-bed").

12. Process according to one of Claims 1-11, characterized by the fact that glycerin is passed, without back-mixing, through the bulk of the catalyst or the reactor tube(s) at a defined residence time.

13. Process according to one of Claims 1-12, characterized by the fact that a mole ratio of hydrogen to glycerin of 2-500 is adjusted, with excess hydrogen being recirculated.

14. Process according to one of Claims 1-13, characterized by the fact that water is removed from the reaction mixture obtained and, if desired, additional processing steps are done.